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Unique, accessible properties, such as high thermal stability, large liquid ranges, high heats of formation, and low to negligible volatility, have led to increased efforts to utilize ionic liquids (ILs; salts with melting points below 100 °C) to replace currently used energetic materials to promote safety and decrease environmental hazards.[1] Our initial strategies have focused on independent design of either ion to tune the physical and chemical properties of ILs;[2,3] however, often the prospective energetic ionic liquids (EILs) suffer from low energetic densities and heat of combustion.[4,5] Nanoparticles, of certain elements, might provide increased energetic density and higher heats of combustion by increasing the overall energy of the system far beyond the heat of formation of the typical products of combustion without further increasing the volume of the system. Incorporation of the correctly chosen nanoparticle additives can lead to a variety of performance improvements, such as decreased ignition delay, decreased burn time, and higher density impulse.

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COMMUNICATION

Tuning azolium azolate ionic liquids to promote surface interactions with titanium nanoparticles leading to increased passivation and colloidal stability†

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The passivation and stability of suspensions of titanium nanoparticles in azolium azolate ionic liquids can be tuned by introducing metal specific binding sites in the azolate anion.

Unique, accessible properties, such as high thermal stability, large liquid ranges, high heats of formation, and low to negligible volatility, have led to increased efforts to utilize ionic liquids (ILs; salts with melting points below 100 °C) to replace currently used energetic materials to promote safety and decrease environmental hazards.[1] Our initial strategies have focused on independent design of either ion to tune the physical and chemical properties of ILs;[2,3] however, often the prospective energetic ionic liquids (EILs) suffer from low energetic densities and heat of combustion.[4,5] Nanoparticles, of certain elements, might provide increased energetic density and higher heats of combustion by increasing the overall energy of the system far beyond the heat of formation of the typical products of combustion without further increasing the volume of the system.[6] Incorporation of the correctly chosen nanoparticle additives can lead to a variety of performance improvements, such as decreased ignition delay, decreased burn time, and higher density impulse.[7]

ILs have already been found to be excellent solvents for nanoparticle synthesis and suspension as the ions provide a steric and electrostatic stabilizing force to prevent aggregation.[8-10] The use of non-functionalized ILs has led to some success in a variety of applications,[11,12] but the long-term stability is still an unknown factor with many of the ILs contemplated as energetic materials. We, for example,[13,14] demonstrated that boron nanoparticles can act as energetic additives in EILs based on the dicyanamide ([DCA]⁻) anion when correctly passivated through IL interactions along the surface of the nanoparticles. We found that if a non-coordinating cation was utilized, the surface interactions take place with the [DCA]⁻ anion leading to poor hypergolic ignition. This suggested that a methodology was needed to induce more favorable surface interactions with the non-trigger counter ion leaving the active ion free to ignite. These results suggested that if the EIL could be designed to include specific metal-surface coordinative interactions, one might be able to passivate and stabilize the nanoparticle dispersions, while greatly enhancing the energetic density.

Chemically designing the IL to specifically interact with the surface of the nanoparticle *via* coordination would allow one to alter the strength of such an interaction by control of the coordinating functionality. It has been shown that coordination can be utilized to increase the stability and catalytic activity of Rh and Pd nanoparticles in an IL by incorporating phosphine functional groups.[15,16] However, our challenge is greater than simply the stabilization of the nanoparticles. A properly chosen energetic composite system, must maintain the appropriate physical and chemical properties (*e.g.*, high density, low viscosity, large liquid range, high thermal stability) and the unique chemical properties (*e.g.*, hypergolicity, short ignition delay, improved energetic density), while simultaneously passivating and stabilizing the nanoparticle suspension.
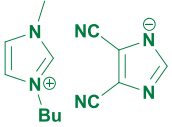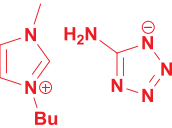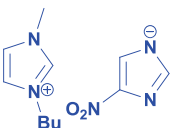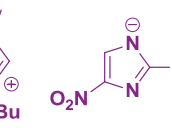
In order to test our hypothesis that coordinative ability of a functional group of an IL ion could be used to tune nanoparticle stability, we chose to investigate a series of azolium azolate ILs (**Table 1**) that had been prepared as part of our EIL project.[17] Azolium azolate based EILs, by incorporation of aromatic nitrogen heterocycles in both cation and anion, have been previously reported to have many favorable energetic properties, such as high thermal stabilities, low melting points, and low viscosities.[18] Here we choose the non-coordinating and commonly used cation, 1-butyl-3-methyl-imidazolium ([BMIM]⁺) to allow focus on the potential coordinating interactions of each type of anion. The azolate anions studied, 4,5-dicyano-imidazolate ([4,5-DiCN-Imid]⁻), 5-amino-tetrazolate ([5-NH₂-Tetra]⁻), 4-nitro-imidazolate ([4-NO₂-Imid]⁻), and 2-methyl-4-nitro-imidazolate ([2-Me-4-NO₂-Imid]⁻), can interact with a metal surface through direct interaction *via* the –CN, –NH₂, and –NO₂ functional groups.

Each of the ILs in **Table 1** was prepared using metathesis reactions with [BMIM][Cl] and the corresponding *in situ* generated potassium azolate salt as described in ref 17. Each IL has the ability to interact though the azolate nitrogen atoms, the π-systems, and a designed interaction through the incorporation of the functional groups on the azolate anion.

Titanium nanoparticles were chosen for this study, due to the

high density (4.51 g/mL) and moderately high heat of combustion (20 kJ/g)[7] of titanium. Based on the high bond dissociation

Table 1. First observable and complete sedimentation times for 100 nm Ti(0) Nanoparticles in AzAz ILs.

Ionic Liquids (prepared as in Smiglak et. al.[17];see ESI)	IL:Ti Molar Ratio	[Ti] (wt%)	T_s/T_f (h)
[BMIM][4,5-DiCN-Imid] η =31.56 cP; ρ =1.080 g/cm^3	100:1	0.186	24/36
	150:1	0.124	24/36
	200:1	0.093	24/36
	250:1	0.075	24/36
[BMIM][5-NH$_2$-Tetra] η =245.3 cP; ρ =1.096 g/cm^3	100:1	0.214	24/72
	150:1	0.143	24/72
	200:1	0.107	36/120
	250:1	0.086	36/120
[BMIM][4-NO$_2$-Imid] η =42.52 cP; ρ =1.201 g/cm^3	100:1	0.190	36/144
	150:1	0.127	48/144
	200:1	0.095	48/168
	250:1	0.076	48/168
[BMIM][2-Me-4-NO$_2$-Imid] η =150.2 cP; ρ =1.134 g/cm^3	100:1	0.180	36/168
	150:1	0.120	48/168
	200:1	0.090	72/168
	250:1	0.072	120/336

[a] Viscosity and Density were determined at 40 °C †

energy of a Ti-O bond (662 kJ/mol), the nitro functional group would be expected to have the highest coordinating ability with two equivalent oxygen atoms available for coordination per IL anion. A Ti-N bond would still provide adequate coordination (462 kJ/mol), which would suggest that the primary amine would provide the second greatest coordinating ability. The cyano functional group would be expected to show the least coordination based on the predicted bond enthalpy and lower nucleophilicity when compared to the primary amine functional group, however, in the dicyano-based anion studied chelation of two cyano groups is possible.[19] The predicted coordinating ability of the functional groups based on the bond dissociation energies is -NO$_2$ > -NH$_2$ > -CN, which, as discussed below and reported in **Table 1** corresponds to our experimental results.

Titanium nanoparticles (d$_{avg}$ = 100 nm) were obtained from Sigma-Aldrich (St. Louis, MO) and separated from the oil stabilizer by washing with freshly distilled *n*-hexane under an Ar atmosphere. The nanoparticles were dried by removal of the *n*-hexane at reduced pressure utilizing Schlenk line techniques and then weighed into vials under Ar in a VAC-Omni Labs (Hawthorne, CA) dry box as a black powder. To remove any remaining volatiles and entrapped gas, the ILs were frozen using a N$_{2(l)}$ bath and allowed to slowly thaw while under high vacuum

(~1 x 10^{-4} torr). This process was repeated to ensure removal of gasses. Next, the predetermined amount of IL was added to the

Fig. 1. [BMIM][4,5-DiCN-Imid] with 0.093 % Ti: (a) before sonication, (b) immediately following sonication, (c) 24 h (T$_s$), (d) 30 h, (e) 36 h (T$_f$).

vials containing the Ti nanoparticles inside the drybox. Four concentrations of Ti in IL were investigated including molar ratios of 100:1, 150:1, 200:1, and 250:1 (IL:Ti), corresponding to Ti concentrations of 0.07 to 0.21 wt%.

The vials were capped, sealed, and removed from the dry box where it was initially observed that the nanoparticles had settled on the bottom of the vials. Vortex mixing and magnetic stirring were unable to disperse the Ti; however, sonication under ambient working conditions, approximately 50 °C as the sonicator naturally provides thermal energy, for 24 h using a Branson 5510 bath sonicator in 99 minute cycles resulted in black colloids with a light green hue around the edge of the vial in each case (**Fig. 1**). NMR spectroscopy of the ILs after sonication did not reveal any degradation products and after sedimentation (discussed below), the ILs had not visibly darkened.

All combinations (**Table 1**) were monitored for colloidal stability and two timescales were recorded: when sedimentation was first observed (T$_s$) and once all of the Ti had settled out (T$_f$, **Fig. 1**). While higher concentrations of Ti were more prone, in general, to sedimentation; the colloidal stability was also related to the coordinative ability of the functional group on the anion, with stability decreasing in the order [2-Me-4-NO$_2$-Imid]$^-$ ~ [4-NO$_2$-Imid]$^-$ > [5-NH$_2$-Tetra]$^-$ > [4,5-DiCN-Imid]$^-$. The [BMIM][2-Me-4-NO$_2$-Imid] colloid (100:1) was stable for at least five days, compared to only 36 h for the 100:1 [BMIM][4,5-DiCN-Imid] colloid. Importantly, any settled particles were easily resuspended by a 3 to 5 min vortex mixing cycle and upon resuspension exhibited the same colloidal stability as noted in **Table 1** for all tested samples. This indicates that the sedimentation is reversible after the initial sonication step suggesting that an initial IL:Ti surface interaction is formed.

Sedimentation was not related to the viscosity or density of the neat ILs. As reported in **Table 1**, [BMIM][5-NH$_2$-Tetra] was reported to have the highest viscosity of the four ILs prepared, but only the third highest dispersion stability. Higher densities seemed to correspond to higher stabilities, but this was not a direct trend. The data suggests a chemical stability mechanism is responsible for the increased dispersion stability and not differences in physical properties.

The increased stability of the colloids formed with ILs containing a nitro group, suggest that specific surface interactions with Ti(0) are responsible for the observed trends. To test this hypothesis, TiO$_2$ (rutile) particles (< 100 nm) were added to each of the four ILs originally studied; however, in these experiments colloids could not be formed. A white mixture was initially created after sonication with all four ILs, but rutile particles rapidly settled out on the order of minutes in all cases. This result suggests that the surface of the Ti(0) nanoparticles discussed above were not fully surface oxidized upon initial incorporation into the EILs.

To determine whether the added functional groups on the azolate anion were chemically interacting with the Ti(0) particles, infrared (IR) spectra of the colloids were compared to neat IL
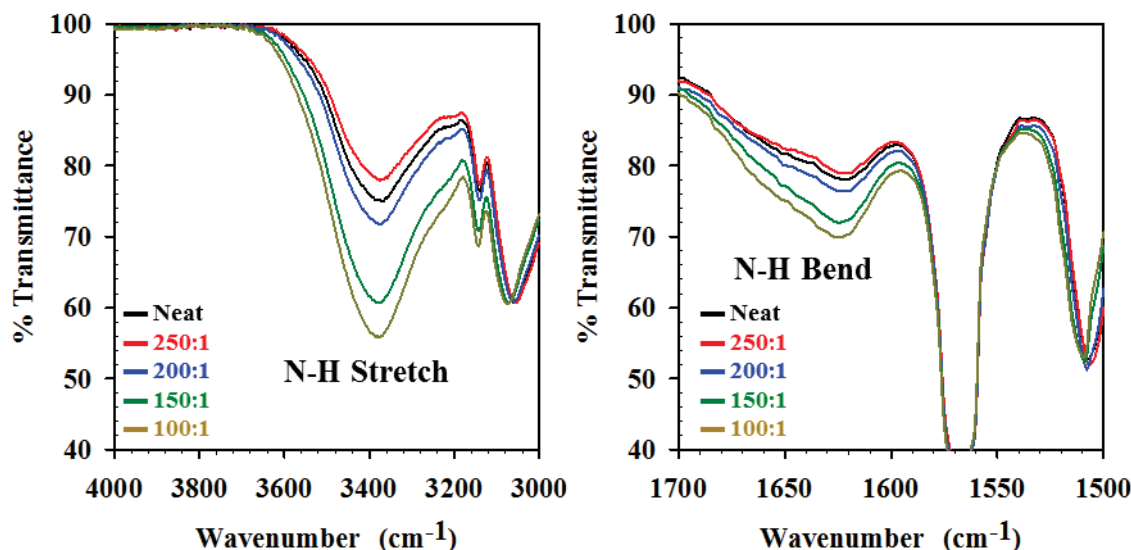
samples. (Full spectral details for all IL samples containing Ti can be found in the ESI.) The least stable colloids containing [BMIM][4,5-DiCN-Imid] did not show any new or shifted bands and were essentially identical with or without Ti.

Addition of Ti(0) nanoparticles to [BMIM][5-NH$_2$-Tetra] resulted in enhanced and increased absorbance for the N-H stretching (~3370 cm^{-1}) and the N-H bending (~1620 cm^{-1}) modes (**Fig. 2**) compared to the neat IL. This increase in absorption does not appear to be proportional to nanoparticle concentration and may result from a surface enhancement effect. It has been theorized that aggregates of nanoparticles can enhance IR absorption in the mid-IR range.[20] If this effect is responsible for the increase in absorption of the N-H stretch it is also consistent with the amine functional group donating, as the N-H bonds will be closest to the surface and thus more strongly affected by the surface enhancement. The Ti surface should act as an electropositive reducing agent since the Ti surface would donate electron density to the protons attached to the amine as well as receiving net electron density from the Lewis basic amine functional group. The results presented in **Fig. 2** indicate a potential Surface Enhanced IR absorption effect with no net shift of the N-H stretch and bend vibrational modes, suggesting that the surface of the Ti nanoparticle is at least partially unoxidized and coordinating with the amine functional group, which acts to further stabilize the [BMIM][5-NH$_2$-Tetra] Ti dispersions.

In addition, the IR spectra indicate the appearance of a new peak at 1650 cm^{-1}, 90 cm^{-1} higher in energy than the –NO$_2$ symmetric stretch at 1560 cm^{-1} (**Fig. 3**). In order to study this peak in more detail, a sample of the 100:1 colloid was concentrated by removing most of the neat IL once the Ti nanoparticles had sedimented to the bottom of the vial. The resulting concentrated sample was redispersed in the remaining IL and analyzed by IR, which indicated a larger relative stretch at 1650 cm^{-1} (**Fig. 3**). This peak corresponds to that expected for a nitroso (R-N=O) functional group, which is a reduced form of a

nitro group. With the relatively high oxophilicity of the Ti(0) surface, it is not unreasonable to suggest the formation of a new Ti-O bond through the nitro functional group that can act to stabilize the nanoparticles. Others have already shown that the formation of Ti-C bonds, a relatively weak bond compared to Ti-O based on bond enthalpy, can help stabilize Ti nanoparticles in dispersion.[21] Reduction of a nitro group to a nitroso group has been reported using a Ti(0) slurry in nitrobenzene.[22]

In order to further investigate the interactions suggested by IR, X-ray Photoelectron Spectroscopy (XPS) was utilized to study the surface of the nanoparticle systems *in situ*. The inherent non-volatility of the ILs we studied allowed us the opportunity to directly study the colloidal solutions under Ultra-High Vacuum (UHV) conditions.[23-25] Samples were applied as liquid droplets (either neat or as dispersions containing Ti nanoparticles) to Cu coated discs and brought under UHV (< 1 x 10^{-9} torr) to perform the XPS experiments. A more stable sample with a coordinating IL, [BMIM][4-NO$_2$-Imid], and a less stable sample with the less coordinating, [BMIM][4,5-DiCN-Imid], were investigated.

The XPS spectra of [BMIM][4,5-DiCN-Imid] with and without Ti were identical and no Ti peak was observed (see ESI). This suggests that in the time needed to prepare the samples for measurement (~2-3 h), the nanoparticles had sedimented and were no longer freely dispersed.

The more stable colloid of [BMIM][4-NO$_2$-Imid] loaded with Ti(0) at a molar ratio of 100:1, however, did provide some interesting results. As shown in **Fig. 4a**, a titanium peak is visible suggesting that the Ti nanoparticles are freely dispersed in the IL and able to access the very top of the droplet as XPS only probes the top 2-5 nm of the droplet. The Ti $2p_{3/2}$ peaks indicate oxidation at the surface accessible to the XPS probe.

The O $1s$ spectrum (**Fig. 4b**) of the neat IL exhibits a single oxygen peak corresponding to the two equivalent oxygen atoms in the nitro functional group of [BMIM][4-NO$_2$-Imid]. In the colloidal sample, a second O $1s$ peak at 531 eV, appears in the

appropriate range for a titanium oxygen bond.[26] This may be indicative of the coordinated, reduced nitro oxygen atom.

Fig. 4c, focused on the N 1s spectra, also shows evidence of reduction through interaction with Ti where three distinct peaks
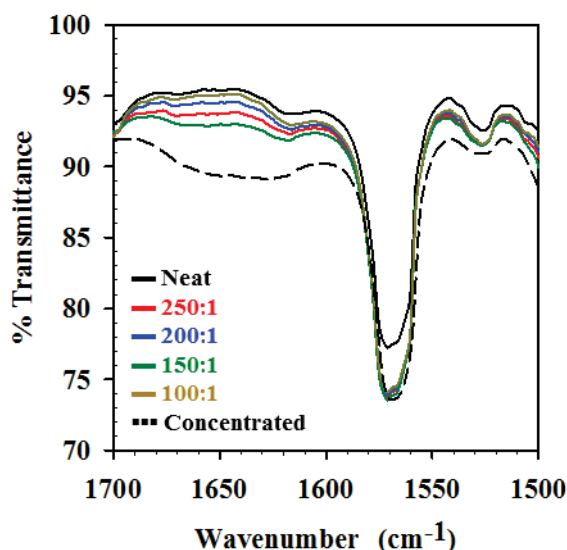
Fig. 3 Appearance of nitroso bands (*ca.* 1650 cm^{-1}) in the IR spectra of [BMIM][4-NO$_2$-Imid] Ti(0) colloids.

are visible. The N atom at the highest binding energy corresponds to the nitrogen in the nitro group, which carries a formal positive charge. The peak at 403 eV can be attributed to the two equivalent nitrogen atoms in the cation, [1-butyl-3-methylimidazolium]$^+$. Two equivalent nitrogen atoms in the azolate anion can be assigned to lowest binding energy present in the neat spectrum, 399 eV. The N 1s peaks for the Ti dispersion match with those of the neat IL, which is consistent with our proposed mechanism that the oxygen atom of the nitro group is reduced, and ring nitrogen atoms are not involved. The lowest binding energy peak which only appears in the Ti dispersion is likely nitride impurity which was initially on the surface.[26]

Thermogravimetric analyses (TGA) were conducted to determine the passivation and oxidation of the Ti(0) particles dispersed in the ILs. The TGA data could be separated into two types of decomposition pathways: compounds without a nitro functional group and compounds that contained a nitro functional group. **Fig. 5** (left) compares the degradation of [BMIM][5-NH$_2$-Tetra] neat and with 100:1 IL:Ti, representing the less stable colloids without nitro groups. The neat sample was fully degraded by 700 °C, while the Ti loaded sample when studied in an air atmosphere gained mass after the IL degraded suggesting Ti oxidation. However, when the sample was studied in an Ar atmosphere, no mass gain was observed. Thus, while the XPS data indicates a possible oxidized Ti surface, the TGA results indicate that at least a portion of the surfaces of the nanoparticles are unoxidized. Similar results were observed for all the ILs studied; even the [BMIM][4,5-DiCN-Imid] system (See ESI).

For the ILs containing the more strongly coordinating anions and producing the more stable colloids, [BMIM][4-NO$_2$-Imid] and [BMIM][2-Me-4-NO$_2$-Imid], the TGA results (**Fig. 5**, right) suggested not only that the surfaces were at least partially

unoxidized, but that there was a new degradation pathway for the nitro groups in the anion, again suggesting surface coordination.

Typically, ILs containing nitro functional groups exhibit a two-step decomposition[27] associated with the degradation of the nitro functional group into an NO$_2$ radical by bond homolysis from a
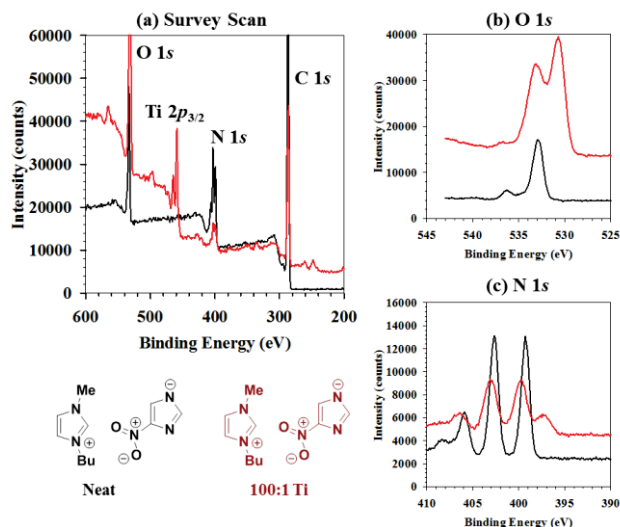
Fig. 4 XPS spectra of [BMIM][4-NO$_2$-Imid] neat and 100:1 with dispersed Ti(0): (a) survey scan, (b) High Resolution O 1s, (c) High Resolution N 1s

heterocycle.[28] The second decomposition step observed in our nitro containing ILs was assigned to the NO$_2$ group based on the theoretical percent molecular weight of the radical NO$_2$ group relative to the molecular weight of the entire IL structure (18%). However, when the Ti-loaded nitro-derivatized ILs were analyzed, the second decomposition step occurred at an elevated temperature when under an Ar purge, but at the same temperature as the neat IL when using an air purge. This data further suggests direct interaction of the nitro groups with the Ti surface, which in the presence of ambient air will be disrupted by the reaction of Ti with O$_2$.

In total, the results presented here suggest that EILs can not only stabilize metallic nanoparticles through the steroelectronic effects of the individual ions,8 but that they can chemically interact with the surface of nanoparticles *via* specific ions as well. Based on the IR, XPS, and TGA data, we suggest stabilization of the Ti(0) particles *via* reaction with the nitro groups resulting in Ti-O bond formation. Ti(0) donates electronic density to the nitro functional group that allows for a reduced oxygen atom to bind to the newly oxidized Ti surface. This new interaction stabilizes the nanoparticle dispersion, allowing for easy resuspension and decreased sedimentation.

Azolium azolate ILs can be functionalized to control and increase the stability of suspensions of Ti(0) nanoparticles by adding specific groups to coordinate or interact with the surface metal *via* only one ion as determined here via IR, XPS, and TGA analysis of the loaded colloids. This approach also leads to surface passivation and safer/easier handing of these particles, while leaving the counterion free to, for example, ignite in a hypergolic reaction. This approach should be applicable to a wide variety of metal nanoparticles by specifically tuning the chemistry of the IL to the surface chemistry of the nanoparticles.

The ability to increase the stability of nanoparticles is crucial to the use of nanoparticles as energetic additives, as a catalyst, or in a variety of specialized applications. The 5-7 day stabilities observed here, however, must be further increased to allow for infinitely stable nanofluid systems for energetic materials and these efforts are currently under way in our laboratories.
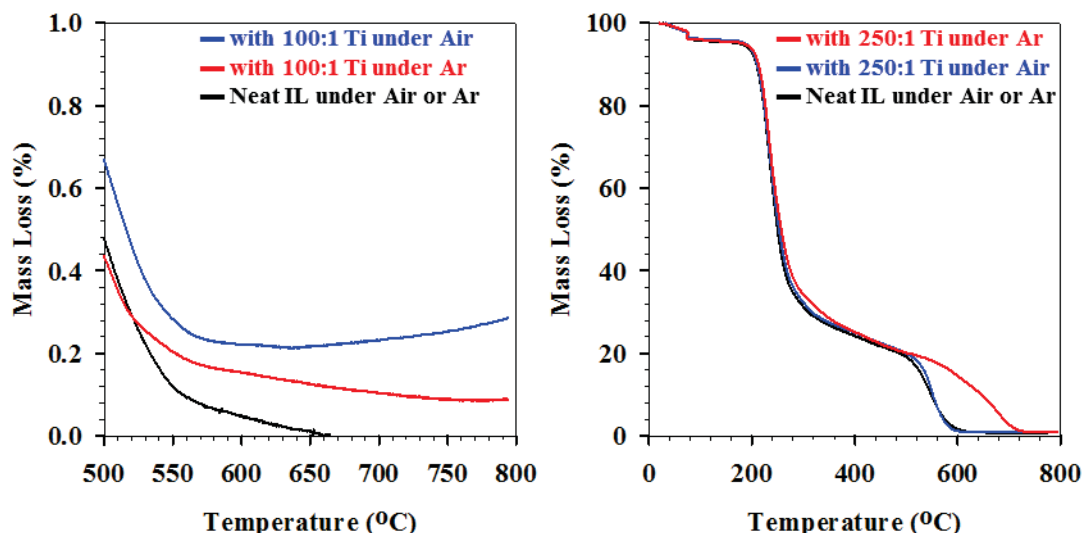

Fig. 5 TGA data for neat and loaded [BMIM][5-NH$_2$-Tetra] (left) and [BMIM][4-NO$_2$-Imid] (right).

Notes and references

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